REACTION OF
1,1-DIPHENYL-2-NITROETHYLENE
WITH STRONG BASE

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August, 1960

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

I. INTRODUCTION

Much interest has been generated in the recent literature concerning the reaction of diphenylvinyl halides with strong base to produce tolans.
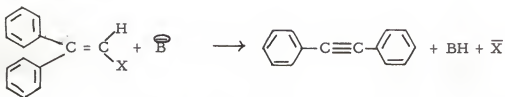
It has been suggested[1] that the reaction involves a rate determining proton transfer followed (or accompanied) by rearrangement and loss of halide. It has been definitely shown that this reaction does not proceed by way of a carbene.[2, 3]

It was thought that it would be of interest to study this type reaction with a compound having the same general structure, but which contained a more electronegative substituent than a halogen. For this purpose 1,1-diphenyl-2-nitroethylene was chosen.

1,1-diphenyl-2-nitroethylene was first prepared by Anschutz and Romig[4] by treating hot acetic acid solutions of either 1,1-diphenylethane or 1,1-diphenylethylene with nitric acid, but the product was erroneously reported as the nitrite ester. Wieland

1

and Rahn[5] showed the true structure by the elimination of nitrous acid from 1,1-diphenyl-1,2-dinitroethane to form the same product. Other workers[6,7] were able to obtain the expected reduction products from this nitro compound.

Lipp and co-workers[7] also treated 1,1-diphenyl-2-nitroethylene with ethanolic potassium hydroxide and obtained benzophenone and nitroacetic acid. They attributed the formation of nitroacetic acid to a known self-condensation of nitromethane in basic media.[8]

II. DISCUSSION

The reaction of 1, 1-diphenyl-2-nitroethylene(I) with potassium
t-butoxide has been found in the present study to produce, as the
major products, benzophenone(III), 1, 3-dinitro-2, 2-diphenylpropane(V),
and 1, 1, 4, 4-tetraphenylbutatriene(IX).

These products can be most readily accounted for on the basis
of competing reactions. The discussion will therefore be divided
into two parts. The first section will deal with the mode of formation
of benzophenone and 1, 3-dinitro-2, 2-diphenylpropane, followed by a
discussion of the formation of 1, 1, 4, 4-tetraphenylbutatriene.

A. The Formation of Benzophenone and 1, 3-Dinitro-2, 2-Diphenylpropane

In the introduction mention is made of the fact that Lipp and co-
workers[7] treated 1, 1-diphenyl-2-nitroethylene with ethnolic potassium
hydroxide at reflux temperature and realized as products benzophe-
none and nitro-acetic acid. Cognizance of this work and that of
Kohler,[9] who has shown that the nitromethane anion adds to
α, β -unsaturated olefins containing a conjugated electron with-
drawing substituent, might suggest an explanation for the formation
of the predominant products in our reaction by the following sequence
of steps:

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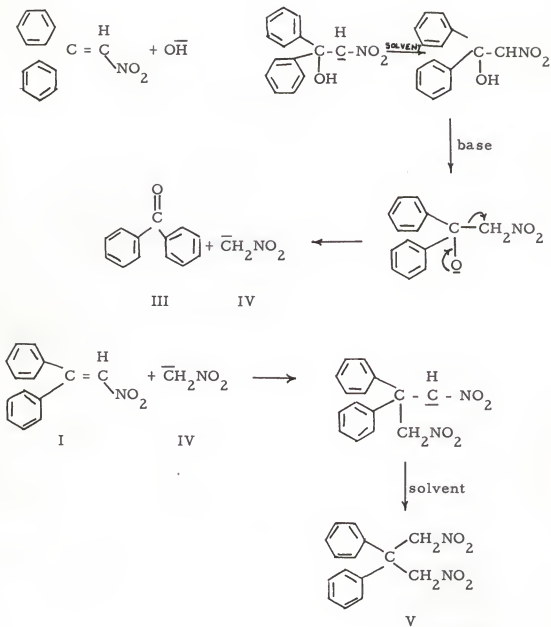
It was felt that there are strong objections to this scheme, however, in that these products were obtained when the reaction was effected in solvents distilled from sodium, using freshly prepared dry potassium $\underline{t}$-butoxide. It can be seen from the reaction scheme that at least one mole of water would be required for each mole of

1,1-diphenyl-2-nitroethylene that underwent this particular reaction. Since yields of 1,3-dinitro-2,2-diphenylpropane as high as 31% have been realized under the anhydrous conditions described in the experimental section, it seems unlikely that hydroxide ion is the attacking nucleophile. Furthermore, when the reaction is run using phenyl lithium as the base, the starting material remains intact. Substitution of phenyl lithium for potassium t-butoxide should certainly have no diminishing effect on the amount of hydroxide present due to any moisture inadvertently incorporated in the reaction mixture.

A more satisfactory explanation would seem to involve the β-addition of the butoxide ion to 1,1-diphenyl-2-nitroethylene followed by a series of reactions analogous to those shown for the hydroxide ion. This sequence may be represented as follows:
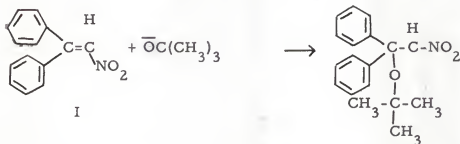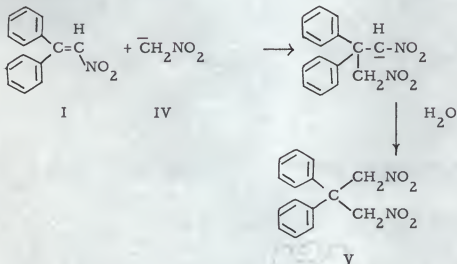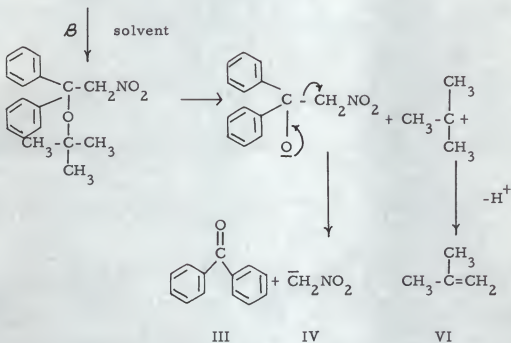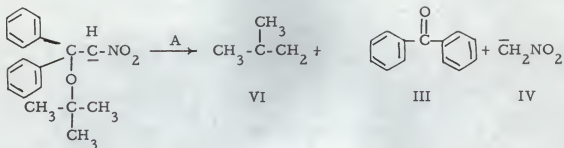
As can be seen from the reaction scheme there are two reasonable paths (A and B) for the adduct of t-butoxide ion and 1,1-diphenyl-2-nitroethylene to undergo decomposition to benzophenone(III), isobutylene(VI), and nitromethane anion(IV). One of these involves the protonation of the adduct and the other involves a concerted decomposition, possibly via a six membered ring transition state.
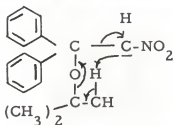
The observation that this reaction proceeds in the absence of a protolytic solvent might be thought to favor the concerted process; however, since only a catalytic amount of some proton donor need be present, this evidence is inconclusive. Some interesting data was obtained in the identification of isobutylene by gas chromatography. It was found that a sample of the spent reaction mixture does indeed contain isobutylene[*] and moreover there appears to be no other butene isomers present. The reaction of t-butyl alcohol with sulfuric acid has been shown to give three separable gaseous

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[*]Isobutylene was identified by comparing the gas chromatograph of the reaction mixture to that of a known sample of isobutylene, as reported in the experimental section.

components, presumably butene isomers formed from an intermediate t-butyl carbonium ion. Since our reaction mixture shows the presence of only isobutylene, it appears that this reaction does not proceed through a free carbonium ion. This could lead to the conclusion that the decomposition proceeds through some cyclic intermediate in which the t-butyl group has no opportunity to rearrange; however, this has not been established.[*]

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[*] The observed products might also arise from the β-addition of the vinyl carbanion to the starting material followed by attack of the t-butoxide ion.
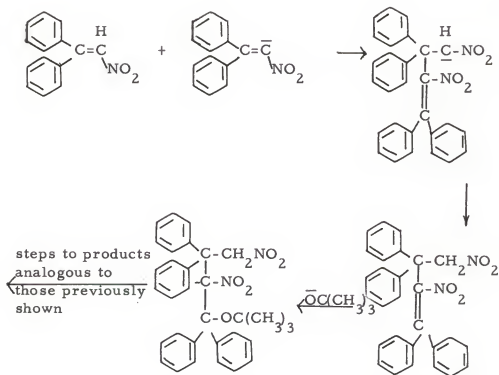
This mechanism is obviously not operative in dilute solution since a 100% yield of benzophenone was realized.

It is readily discernible that this reaction requires more investigation especially in view of its potential synthetic value. This work was primarily concerned with the formation of 1, 1, 4, 4-tetraphenylbutatriene(IX) and therefore this portion of the study was left at this point.

B. The Formation of 1, 1, 4, 4-Tetraphenylbutatriene

The overall reaction to produce 1, 1, 4, 4-tetraphenylbutatriene from 1, 1-diphenyl-2-nitroethylene(I) may be written as follows.

$$+ 2 (CH_3)_3COH + 2 KNO_2$$
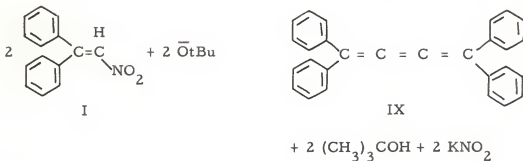
This reaction appears to be similar to the reaction of 9-halomethylenefluorenes with strong bases to produce the analogous 1, 4-dibiphenylenebutatriene which has received considerable discussion in the recent literature.[10, 11]

Two reasonable mechanisms have been postulated to account for the formation of cumulenes in this type reaction, one involving a carbene intermediate and the other an "addition-elimination" mechanism.

Curtin[10] has discussed the possibility of an intervening carbene in some detail. An analogous mechanism in this system might be described as follows. In the first step there is an acid-base re-action involving 1, 1-diphenyl-2-nitroethylene(I) and potassium t-butoxide to produce the corresponding vinyl carbanion(VII) and t-butyl alcohol:
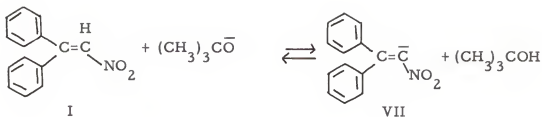
The vinyl carbanion(VII) could lose nitrite ion to form diphenylvinyl carbene(X).
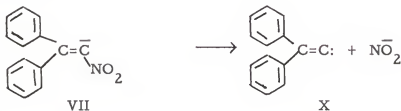
This carbene could then follow any one of three paths toward the formation of 1, 1, 4, 4-tetraphenylbutatriene(IX).

(1) Two carbenes could undergo coupling:
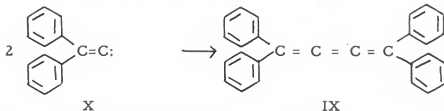
(2) The carbene could attack the original 1, 1-diphenyl-2-nitro-ethylene(I) with the formation of a cyclopropane intermediate which, in the basic reaction mixture, could lose the elements of nitrous acid and undergo ring opening to form the triene:[12]
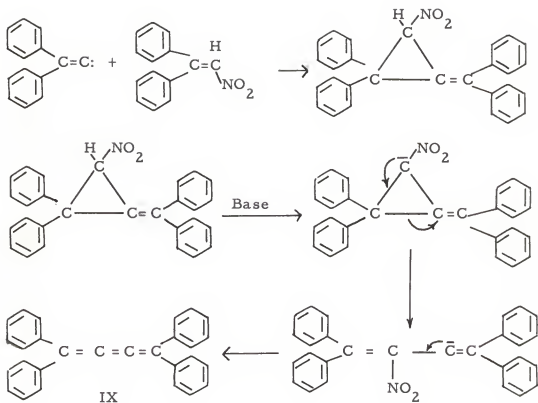
(3) The electrophilic carbene could react with the vinyl carbanion produced in the first step to form an intermediate which could lose nitrite ion to form the triene.
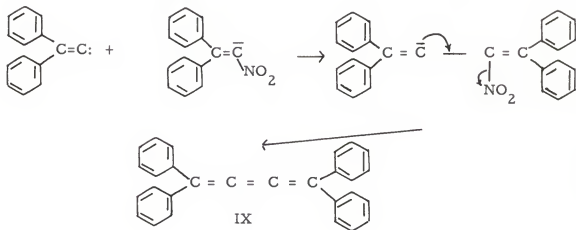
The carbene coupling route appears unlikely due to the extremely low concentration of such a high energy intermediate.

The attack of a carbene on the 1, 1-diphenyl-2-nitroethylene(I) can also be questioned on the grounds that a double bond conjugated with an electron withdrawing substituent, such as the nitro group, would be expected to undergo comparatively slow reaction with a carbene. In support of this argument Doering and Henderson[13] have shown that carbenes, generated from haloforms and potassium t-butoxide, react most rapidly with olefins which can readily support a positive charge. For example they have shown that tetra-substituted alkyl olefins react faster with carbenes than do tri-substituted alkyl olefins which react faster than do di-substituted alkyl olefins. Hine and co-workers[14] have shown that dichlorocarbene reacts more rapidly with alkoxide ions than it does with ethylene, which is another implication that olefins which cannot readily support a positive charge react slowly with carbenes.

Thus, if a carbene intermediate is operative, its most plausible path to the triene is by way of attack on the vinylcarbanion(VII) followed by loss of nitrite ion.

The other mechanism offered for this type of replacement has been discussed fully by Truce and co-workers[15] and by Hauser and Lednicer[11] and may be shown in this system as follows.

Again the first step would involve the removal of a proton from
1, 1-diphenyl-2-nitroethylene(I) by the basic potassium t-butoxide
to form the vinyl carbanion(VII).
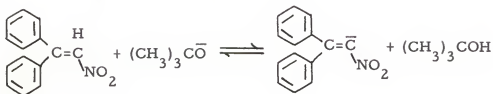
The vinyl carbanion could then add to the original olefin alpha to the
nitro group to produce a dinitro intermediate carbanion which could
lose nitrite ion to produce an intermediate substituted butadiene(XI).
This in turn could undergo base catalyzed beta elimination of
nitrous acid to produce 1, 1, 4, 4-tetraphenylbutatriene(IX) as shown
below:
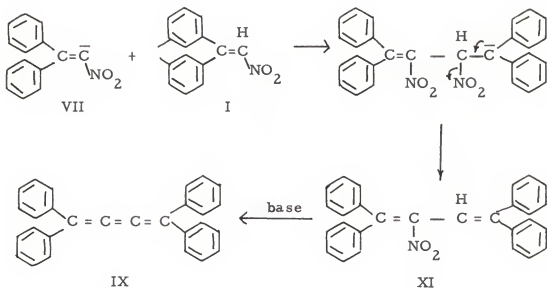
This mechanism is closely analogous to the one proposed for the conversion of α-phenyl alkyl halides to dimeric olefins,[16,17] in which expected intermediates have been isolated and shown to go on to olefinic products. For example in the reaction of benzhydryl chloride with sodamide to produce tetraphenylethylene, the intermediate 1, 1, 4, 4-tetraphenyl-1-chloroethane was isolated in 60% yield and shown to proceed on to olefinic products almost quantitatively. The production of the above intermediate involves the displacement of a negative ion from an sp^3 carbon atom; whereas, in this system the loss of a negative ion from an sp^2 carbon atom would be involved. The mechanistic differences between these types of displacement have been discussed by Truce and co-workers.[15]

One means of eliminating carbene coupling as a possible path for product formation would be the isolation of an intermediate analogous to the one prepared by Kharasch,[16] i.e.

XI
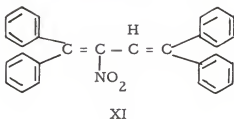
Accordingly experiments were undertaken to accomplish this; however, they were unsuccessful as is reported in the experimental section. It can be seen from the mechanistic schemes that this failure places

limits only on the discussion of the carbene coupling path, since all the other routes lead through either the compound above (XI) or its anion.

A general approach to the problem of differentiating between a mechanism involving a carbene intermediate and one involving an "addition-elimination" process might well be the addition of some carbene acceptor species to the reaction mixture. This additive should be some compound whose reaction product, with the carbene in question, would be characterizable.

Several investigators[13, 14, 18] have reported on the reactivity of carbene intermediates with olefins. Cyclohexene was chosen in the present work due to its availability and relatively high boiling point. Results of several attempts to isolate an identifiable product using cyclohexene as the solvent were inconclusive in that discoloration and apparent decomposition occurred in the reaction mixture. However, two runs, differing only in that one contained a one hundred molar excess of cyclohexene, showed no difference in the amount of 1, 1, 4, 4-tetraphenylbutatriene(IX) formed. The addition of a concentrated solution of potassium t-butoxide in t-butyl alcohol to 1, 1-diphenyl-2-nitroethylene(I) dissolved in heptane afforded a 2.3%[*] yield of triene. The addition of the same solution to

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[*]This was determined from the ultraviolet spectrum. For details see the experimental section.

1,1-diphenyl-2-nitroethylene(I) dissolved in heptane containing a
one hundred molar excess of cyclohexene gave the same 2.3% yield
of triene. If a carbene intermediate were operative in this case,
it would be required to couple at a vanishingly low concentration,
interact with the vinyl carbanion, or react with the deactivated
double bond of the original olefin much more rapidly than it reacts
with the large excess of cyclohexene.

Bamford and Stevens[19] have shown that carbenes react with
organic bases in a typically electrophilic manner. Another attempt
to isolate some distinctive product from reaction of a carbene inter-
mediate was the reaction of 1,1-diphenyl-2-nitroethylene(I) with
potassium t-butoxide in the presence of a one hundred molar ex-
cess of diethylamine(XII). If any diphenylvinyl carbene were present
and behaved analogously to those of Bamford and Stevens,[19] it
would have produced N,N-diethyl-β,β-diphenylvinylamine (XIII)
as shown in the following sequence of reactions:

XIII
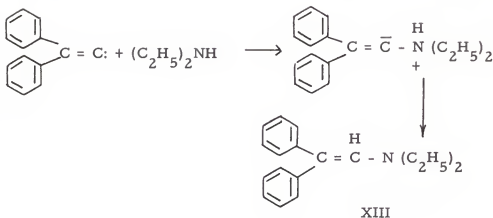
Work up of the reaction mixture afforded no such basic material. Comparative runs were again made, and it was found that the presence of the nucleophilic amine has no effect on the amount of triene formed.

Other attempts to capture the carbene included the addition of ammonia, the addition of aniline, and the addition of thiophenoxide ion to the reaction mixture. All these experiments failed to yield the expected products.

It is felt that the evidence cited heretofore is a strong indication that the carbene mechanism is not operative in this reaction.

In order to demonstrate that the initial step in this reaction does indeed involve the removal of a proton from the nitro-olefin with the resulting formation of a carbanion, identical runs of the reaction were made except that in one of the reaction mixtures there was included a tenfold excess of methyl iodide. The mixture containing methyl iodide showed a 40-50% drop in the amount of triene formed. Another pair of runs was made in which there was included in the reaction mixture containing methyl iodide enough excess potassium t-butoxide to completely react with the methyl iodide and still retain the same mole ratio of 1, 1-diphenyl-2-nitro-ethylene(I) to potassium t-butoxide as was present in the blank. These runs gave the same 40-50% drop in the amount of triene formed. *

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*See Table IV of the experimental section.

This is consistent with the removal of the vinyl carbanion by a dis-
placement of iodide from methyl iodide and consequently, the amount
of carbanion which can proceed to triene.

Another indication of the presence of a carbanion during the
course of the reaction is the necessity of using a strong base such
as t-butoxide ion.

It is therefore suggested that this dimerization reaction pro-
ceeds by the formation of a vinyl carbanion which in turn adds to the
original 1, 1-diphenyl-2-nitroethylene. This addition product then
goes through β-elimination steps to arrive at the final product,
1, 1, 4, 4-tetraphenylbutatriene.

Mention should be made of the fact that we attempted to effect
this reaction using other bases, notably phenyl lithium and sodamide,
without success.

III. EXPERIMENTAL

1,1-Diphenylethylene. — 1,1-Diphenylethylene was prepared from bromobenzene and ethyl acetate by the method of Allen and Converse[20] as reported in Organic Syntheses.

1,1-Diphenyl-2-nitroethanol. — 1,1-Diphenyl-2-nitroethanol was prepared by an adaptation of the method of Anschutz.[4]

A solution of 21.1 grams (0.12 moles) of 1,1-diphenylethylene in 150 ml. of acetic acid was cooled to 5° in an ice-water bath. To this solution 8 ml. of nitric acid (Sp. Gr. 1.42; 0.12 moles) was added dropwise with stirring. The solution was allowed to stand at room temperature overnight and then heated on a steam bath for seven hours. At the end of this period the dark red solution was poured over crushed ice giving a dark oily mass. Recrystallization of a small portion of this product from pentane afforded a colorless crystalline product, m.p. 106-107° (lit.[4] 106-107°).

1,1-Diphenyl-2-nitroethylene(I). — This compound was prepared by an adaptation of the method of Wittig and Gauss.[21]

The crude 1,1-diphenyl-2-nitroethanol previously prepared was dissolved in ether, the solution dried over anhydrous magnesium sulfate, filtered and the solvent removed on a steam bath. The

residue was dissolved in 100 ml. of glacial acetic acid, and 9.4 grams

(0.12 moles) of acetyl chloride was added. This solution was refluxed

for three hours at which time it was poured over crushed ice, yielding

a dark oil. Recrystallization from hexane gave 8.9 grams (33%) of

yellow crystals, m.p. 86-87° (lit.[4] 86-87°).

1,1,4,4-Tetraphenylbutatriene(IX). — This compound was prepared

from 0.5 grams (1.3×10^{-3} moles) of 1,1,4,4-tetraphenyl-2,3-

dihydroxybutyne-2[22] by addition to 50 ml. of previously prepared

3% hydroiodic acid in glacial acetic acid solution* which had been

cooled to 0° in an ice-salt bath. The solution was maintained at

this temperature for seven hours at which time it was added to

200 ml. of cold water. A yellow solid separated which was filtered

and recrystallized from ethyl acetate to give 0.39 grams (85%)

of IX, m.p. 236-237°, (reported[23] m.p. 236°).

1,3-Dinitro-2,2-diphenylpropane(V). — To 25 ml. of methyl alcohol

which had been saturated with solid potassium hydroxide was added

0.37 grams (1.64×10^{-3} mole) of 1,1-diphenyl-2-nitroethylene. To

the resulting solution was added 1.14 grams (1.8×10^{-2} mole) of

nitromethane. The reaction was allowed to proceed for three days

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*This solution was prepared by allowing the fumes from a heated
mixture of phosphoric acid and sodium iodide to pass into glacial
acetic acid until the calculated weight was gained.

at room temperature. After this period of time, the solution was acidified with dilute hydrochloric acid yielding a pale yellow solid. Recrystallization from 95% ethanol gave 0.37 grams (79%) of white crystals, m.p. 201-202°.

1,1-Diphenyl-1-methoxy-2-nitroethane. — To 25 ml. of methyl alcohol which had been saturated with solid potassium hydroxide was added 0.37 grams (1.64×10^{-3} mole) of 1,1-diphenyl-2-nitroethylene. The resulting solution was allowed to stand for three days at which time it was neutralized with dilute hydrochloric acid yielding a pale yellow solid. Recrystallization from ethanol and water gave 0.36 grams (88%) of a white compound, m.p. 140-141°, (lit.[24] 139°).

Analysis: Calculated for $C_{15}H_{15}NO_3$; C, 70.05; H, 5.83; N, 5.47. Found: C, 70.39; H, 5.78; N, 5.60.

Preparation of Basic Reagents. — Solutions of potassium t-butoxide in t-butyl alcohol were prepared as follows.

To a 3-necked flask fitted with a stirrer, calcium chloride drying tube, and an inlet for dry nitrogen was added t-butyl alcohol which had been freshly distilled from sodium metal. While being continually swept with dry nitrogen, small pieces of potassium metal, cut under hexane, were added to the contents of the flask. The flask was immediately stoppered and stirred under the nitrogen atmosphere until reaction of the potassium metal was complete. The concentration of t-butoxide ion was determined by placing an aliquot of

the above solution in water and titrating with standard acid using phenolphthalien as the indicator.

Dry potassium t-butoxide was prepared as follows: To a 3-necked flask fitted with a stirrer, condenser (with a calcium chloride drying tube) and an inlet for dry nitrogen was added either xylene or toluene freshly distilled from sodium metal. To the contents of the flask was added potassium metal cut into small pieces under hexane. The temperature was raised to the reflux point and to the suspension of molten potassium droplets was added dropwise one molar excess of t-butyl alcohol which had been freshly distilled from sodium metal. The mixture was refluxed for two hours after addition of the alcohol was complete and filtered under nitrogen. The residue was washed thoroughly with sodium dried ether and dried in a vacuum dessicator.

Phenyl lithium was prepared by the method of Evans and Allen.[25]

Reaction of 1, 1-Diphenyl-2-nitroethylene(I) with a Solution of Potassium t-Butoxide in t-Butyl Alcohol. — A solution of 4.0 grams (1.8×10^{-3} mole) of 1,1-diphenyl-2-nitroethylene(I) in 100 ml. of t-butyl alcohol (freshly distilled from sodium) contained in a 3-necked flask fitted with a stirrer, condenser and dropping funnel was flushed well with dry nitrogen and heated to reflux. To the stirred refluxing solution was added dropwise 0.036 mole of potassium t-butoxide in 50 ml. of t-butyl alcohol over a 30 minute interval. Upon commencement of addition a red color developed in the reaction

mixture. After several minutes a precipitate began to settle out
which remained throughout the reaction period. The reaction was
allowed to proceed for four hours at which time the hot mixture was
filtered through a Buchner funnel giving a water soluble solid resi-
due. Acidification of an aqueous solution of the residue gave 0.8
grams (31%) of white solid. Recrystallization from 95% ethanol
gave pure 1, 3-dinitro-2, 2-diphenylpropane(V), m.p. 201-202°.

Analysis: Calculated for $C_{15}H_{14}N_2O_4$: C, 62.94; H, 4.90;
N, 9.80. Found: C, 63.13; H, 5.11; N, 9.87. Molecular weight:
calculated, 286. Found: 277 (camphor).

The t-butyl alcohol filtrate was then poured into cold water and
allowed to stand for two days after which time a small amount of
yellow solid had precipitated out. This was filtered and recrys-
tallized from ethyl acetate giving yellow crystals of 1, 1, 4, 4-
tetraphenylbutatriene(IX), m.p. 236-237°.

This filtrate was then evaporated under reduced pressure to
give a dark oil. Distillation of this oil at ca. 2mm. of Hg gave
benzophenone. The oxime derivative melted at 140-141°, reported,[26]
m.p. 140°. The distillate and an authentic sample of benzophenone
gave identical infra-red spectra.

Identification of Isobutylene from the Reaction of 1, 1-Diphenyl-
2-nitroethylene with Potassium t-Butoxide. — The reaction was run
as previously described for the use of t-butyl alcohol solution. After

completion of the reaction period, 5 ml. of the crude reaction mix-
ture was distilled into a cold trap surrounded by a dry ice-acetone
bath. A sample of the gas above the distillate passed through a
Perkin-Elmer vapor fractometer Model 154B at 15 lbs. pressure
and a temperature of 31° using a Perkin-Elmer column B gave a
compound having a retention time of 2.6 minutes. Injection of a
sample of the t-butyl alcohol distillate showed the same compound.
A sample of isobutylene (C.P.) obtained from the Matheson Company
run under identical conditions gave a peak of the same shape at the
same retention time.

Reaction of t-Butyl Alcohol with Sulfuric Acid. — A three-necked
flask containing 100 ml. of concerted sulfuric acid was heated to
160° and freshly distilled t-butyl alcohol (25 ml.) was added
dropwise. The fumes from the reaction mixture were allowed to
pass into a cold trap surrounded by a dry ice-acetone bath. After
the addition was complete, the trap was disconnected from the
reaction flask and connected to another cold trap which had been
immersed in a dry ice-acetone bath. By allowing the original trap
to warm to room temperature distillation of the gaseous product was
effected. Passing this gaseous product through the vapor frac-
tometer under the same conditions as recorded earlier gave three
peaks one of which is identical to that of pure isobutylene, retention
time 2.6 minutes. The other peaks were at retention times of 1.9

and 3.8 minutes. These are probably due to other butene isomers although no attempt was made to determine this.

Reaction of 1,1-Diphenyl-2-nitroethylene(I) with Dry Potassium t-Butoxide. — In a three-necked flask fitted with a stirrer, condenser, and an inlet for dry nitrogen was placed a solution of 2.0 grams $(8.8 \times 10^{-3}$ mole) of 1,1-diphenyl-2-nitroethylene(I) in 150 ml. of dry heptane. The system was flushed with dry nitrogen and heated to the reflux temperature. To this refluxing solution was added 2.0 grams $(1.8 \times 10^{-2}$ mole) of dry potassium t-butoxide in small portions. This was accomplished by use of a addition tube for solids as described by Fieser.[27] After each addition a red color developed in the reaction mixture. The mixture was refluxed for five hours after completion of the addition. It was then filtered, while still hot, through a Buchner funnel. The residue was triturated with 100 ml. of water, filtered, and the filtrate acidified with dilute hydrochloric acid yielding 0.31 grams (24%) of a white solid. Recrystallization from 95% ethanol afforded white crystals (V), m.p. 201-202°. A mixed melting point with the compound isolated from the reaction of nitromethane and 1,1-diphenyl-2-nitroethylene showed no depression.

Upon cooling, the heptane filtrate deposited 0.12 grams (7.6%) of yellow crystals(IX), m.p. 236-237°. A mixture with an authentic sample of 1,1,4,4-tetraphenylbutatriene(IX) showed no depression.

Analysis: calculated for $C_{28}H_{20}$: C, 94.37; H, 5.63. Found: C, 94.12; H, 5.60. Molecular weight: calculated: 356. Found: 370.

Evaporation of the heptane filtrate almost to dryness afforded 0.34 grams (17%) of the starting material (I), m.p. 86-85°. The infra-red spectrum of the residue left after complete evaporation was almost identical to that of benzophenone.

Attempted Isolation of Intermediate Substituted Butadiene(XI). —
In a three-necked flask fitted with a stirrer, condenser, and an inlet for dry nitrogen was placed a solution of 2 grams (8.8×10^{-2} mole) of 1,1-diphenyl-2-nitroethylene(I) in 100 ml. of dry heptane. To the refluxing solution was added dropwise 10 ml. of 0.382 M potassium t-butoxide in dry t-butyl alcohol. The addition required 15 minutes. The mixture was refluxed for four hours after completion of the addition. It was then filtered while still hot through a Buchner funnel. The solid residue was triturated with 100 ml. of water, filtered, and the filtrate acidified with dilute hydrochloric acid yielding 0.33 grams (26%) of a white solid. Recrystallization from 95% ethanol afforded white crystals(V), m.p. 201-202°.

The heptane layer deposited a small crop of yellow crystals(IX) (m.p. 236-237°) upon cooling. Evaporation of the heptane layer almost to dryness gave 0.9 grams (45%) of starting material.

Reaction of Dry Potassium t-Butoxide with 1,1-Diphenyl-2-nitro-ethylene(I) in Cyclohexene Solvent. — 1,1-Diphenyl-2-nitroethylene(I)

(2.0 grams; 8.8×10^{-3} mole) was dissolved in 200 ml. of freshly distilled cyclohexene. The three-necked reaction flask was flushed well with dry nitrogen, and 1.95 grams (1.74×10^{-2} mole) of dry potassium t-butoxide added in small portions[27] to the refluxing solution. The solution was refluxed for four hours after the addition of base was completed. During this time discoloration and apparent decomposition occurred. Filtration of the hot mixture and evaporation of the cyclohexene solvent gave a brown oil which could not be purified. The solid residue was dissolved in water. Acidification with dilute hydrochloric acid gave crude V. Recrystallization from 95% ethanol gave white crystals(V), m.p. 201-202°.

Reaction of 1,1-Diphenyl-2-nitroethylene(I) with Dry Potassium t-Butoxide in the Presence of Diethyl Amine. — 1,1-Diphenyl-2-nitroethylene (2.0 grams; 8.8×10^{-3} mole) was dissolved in 150 ml. of dry heptane. To this solution was added 7.0 grams (9×10^{-2} mole) of diethylamine(XII). The three-necked reaction flask was flushed well with dry nitrogen and 1.95 grams (1.74×10^{-2} mole) of dry potassium t-butoxide added in small portions[27] to the refluxing solution. The mixture was refluxed for four hours after addition of the base was complete and then filtered. Both the filtrate and the residue were extracted with 10% hydrochloric acid. Neutralization of the acid extracts with sodium hydroxide gave no organic product.

Reaction of 1,1-Diphenyl-2-nitroethylene(I) with Potassium t-
Butoxide in the Presence of Sodium Thiophenoxide. — 1,1-Diphenyl-
2-nitroethylene (4.0 grams; 1.76 x 10^{-2} mole) was dissolved in 150 ml.
of t-butyl alcohol, freshly distilled from sodium. To this solution
was added 3.9 grams (2.6 x 10^{-2} mole) of sodium thiophenoxide.
The three-necked reaction flask was flushed well with dry nitrogen
and 3.9 grams (3.5 x 10^{-2} mole) of potassium t-butoxide dissolved in
100 ml. of t-butyl alcohol added dropwise to the refluxing solution.
The solution was refluxed for four hours after the addition was com-
plete and then poured in 500 ml. of water. Filtration of this mix-
ture afforded 2.0 grams of solid which upon recrystallization from
ethanol and water showed m.p. 60-61°. A mixture with authen-
tic sample of diphenyl disulfide showed no depression.

The water filtrate was extracted with ether and the other extract
dried over anhydrous magnesium sulfate. Evaporation of the ether
solvent afforded an oil which distilled at ca. 140° at 2 mm of Hg.
The infra-red spectrum of this liquid was identical to that of benzo-
phenone.

The water layer, upon acidification with dilute hydrochloric acid,
afforded a small amount of white compound, m.p. 243-244°. Analysis
of this product showed no sulfur.

Analysis: C, 70.83; N, 11.13; H, 5.31; S, 0.00.

Reaction of 1,1-Diphenyl-2-nitroethylene(I) with Phenyl Lithium in
Ether Solution. — 1,1-Diphenyl-2-nitroethylene(I) (0.4 grams;
1.8×10^{-3} mole) was dissolved in 100 ml. of ether. The three-
necked reaction flask was flushed well with dry nitrogen, and 7.8 ml.
$(1.8 \times 10^{-3}$ mole) of phenyl lithium in ether were added to the stirred
solution. The mixture was stirred for 10 hours under nitrogen at-
mosphere. During this time a small amount of brown solid separated
out which proved to be water and alcohol soluble. Filtration and
evaporation of the ether solvent afforded 0.34 grams (85%) of the
starting material (I).

The above reaction was run using one mole of 1,1-diphenyl-
2-nitroethylene(I) to two moles of phenyl lithium with the same
results.

Reaction of Phenyl Lithium with 1,1-Diphenyl-2-nitroethylene(I)
in Heptane. — 1,1-Diphenyl-2-nitroethylene(I) (0.5 grams; 2.2×10^{-3}
mole) was dissolved in 100 ml. of dry heptane. The three-necked
reaction flask was flushed well with dry nitrogen and 10 ml.
$(4.4 \times 10^{-3}$ mole) of phenyl lithium in dry ether added dropwise to
the refluxing solution.

The solution was refluxed for four hours after the addition was
complete. Filtration of the reaction mixture and evaporation of the
solvent afforded 0.43 grams (86%) of starting material (I).

Reaction of 1,1-Diphenyl-2-nitroethylene(I) with Sodamide in
Liquid Ammonia. — 1,1-Diphenyl-2-nitroethylene(I) (0.8 grams;
3.6×10^{-3} mole) was dissolved in 25 ml. of dry ether and added to
250 ml. of liquid ammonia in a three-necked flask. A Dewar con-
denser was used to prevent evaporation of the liquid ammonia. To
this stirred mixture 0.3 grams (7.2×10^{-3} mole) of sodamide was
added using a solid addition tube.[27] The mixture was allowed to
stand for four hours and then the solvent removed on a steam bath.
The residue was triturated with 200 ml. of a 2% hydrochloric acid
solution and filtered. Recrystallization from hexane gave 0.6 grams
of the starting material (I), m.p. 86-87°.

Reaction of Sodamide with 1,1-Diphenyl-2-nitroethylene in Heptane. —
1,1-Diphenyl-2-nitroethylene (1.0 gram; 4.4×10^{-3} mole) was
dissolved in 100 ml. of dry heptane. The three-necked reaction
flask was flushed with dry nitrogen and 0.5 grams (1.3×10^{-2} mole)
of sodamide added to the refluxing solution by means of an addition
tube for solids. Refluxing was continued for five hours at which
time the mixture was filtered and the heptane solvent removed
affording 0.98 grams of starting material (I).

Quantitative Determination of 1,1,4,4-Tetraphenylbutatriene(IX),
Benzophenone(III), and Unreacted 1,1-Diphenyl-2-nitroethylene(I). —
Quantitative runs were made utilizing the Beckman DK-2 Spectro-
photometer. For these studies it was necessary to run calibration

curves on all the above compounds. These data are given in Tables 1-3.

In all cases straight lines were obtained when plotting absorbance (A) against concentration, thus all of these compounds follow Beer's Law.

The reactions for quantitative determinations were all run under very similar conditions. The procedure for one of these is given below. The other results are summarized in Table 4.

Reaction of 1,1-Diphenyl-2-nitroethylene(I) with a t-Butyl Alcohol Solution of Potassium t-Butoxide in the Presence of Cyclohexene. —
1,1-Diphenyl-2-nitroethylene(I) (0.02 gram; 8.8×10^{-5} mole) was dissolved in 4 ml. of dry heptane. To this solution was added 1 ml. (1×10^{-2} mole) of cyclohexene. The three-necked flask was flushed with dry nitrogen and 1.0 ml. of a t-butyl alcohol solution of potassium t-butoxide (0.8M) added dropwise by means of a syringe. The solution was refluxed, with constant agitation, for 30 minutes at which time the hot mixture was poured in 30 ml. of boiling chloroform. The solution was washed twice with 50 ml. portions of saturated salt solution and dried over anhydrous magnesium sulfate. The solution was made up to volume in a 50 ml. volumetric flask and the ultra-violet absorption spectrum determined. It was necessary to dilute the solution to 500 ml. in order to observe the spectrum. The absorbance of 0.08 at 420 $m\mu$ corresponds to a

2×10^{-6} molar solution (2.3%) of 1,1,4,4-tetraphenylbutatriene.

The difference in the observed absorbance and the absorbance of a solution of IX at the above concentration gives one the absorbance of 1,1-diphenyl-2-nitroethylene and thus its concentration, 3×10^{-5} molar (14%).

A blank differing from the above reaction only in that 5 ml. of heptane were used as the solvent rather than 4 ml. of heptane and 1 ml. of cyclohexene also gave a 2.3% yield of triene.

TABLE 1

CALIBRATION CURVE DATA FOR
1,1-DIPHENYL-2-NITROETHYLENE

Concentration in moles/liter	A (310 $m\mu$.)	A (360 $m\mu$.)
1.00×10^{-4}	0.770	0.330
8.00×10^{-5}	0.645	0.270
7.00×10^{-5}	0.565	
6.00×10^{-5}		0.200
5.00×10^{-5}	0.410	
4.00×10^{-5}	0.335	0.140
3.00×10^{-5}	0.245	
2.00×10^{-5}	0.150	
1.00×10^{-5}	0.080	0.040

TABLE 2

CALIBRATION CURVE DATA FOR
1, 1, 4, 4-TETRAPHENYLBUTATRIENE

Concentration in moles/liter	A (420 $m\mu$.)	A (360 $m\mu$.)	A (260 $m\mu$.)
2.00 x 10^{-5}	0.765	0.165	0.470
1.40 x 10^{-5}	0.550	0.120	0.345
1.20 x 10^{-5}	0.460	0.105	0.290
1.00 x 10^{-5}	0.390	0.095	0.240
7.00 x 10^{-6}	0.275	0.065	0.180
5.00 x 10^{-6}	0.195		0.130
3.00 x 10^{-6}	0.115	0.030	0.070
1.00 x 10^{-6}	0.040		

TABLE 3

CALIBRATION CURVE DATA FOR BENZOPHENONE

Concentration in moles/liter	A (260 $m\mu$.)
3.00 x 10^{-5}	0.545
2.50 x 10^{-5}	0.445
2.00 x 10^{-5}	0.350
1.00 x 10^{-5}	0.180

TABLE 4

SUMMARY OF EXPERIMENTAL RESULTS

Moles of Nitro-olefin	Moles of Base[a]	Type of Base	Moles of Reagent Added	Reaction Time hrs.	% Nitro-olefin Unreacted	% Yield of Triene
8.8×10^{-5}	8×10^{-4}	KOt-Bu	none	0.5	13	2.3
8.8×10^{-5}	8×10^{-4}	KOt-Bu	1×10^{-2} cyclohexene	0.5	14	2.3
2.2×10^{-4}	8×10^{-4}	KOt-Bu	none	2	14	2.1
2.2×10^{-4}	8×10^{-4}	KOt-Bu	1×10^{-3} diethylamine	2	17	2.1
2.2×10^{-4}	8×10^{-4}	KOt-Bu	none	2	18	4.0
2.2×10^{-4}	4×10^{-3}	KOt-Bu	3.2×10^{-3} methyl iodide	2	16	2.2
2.2×10^{-4}	8×10^{-4}	KOt-Bu	none	1.5	21	5.4
2.2×10^{-4}	8×10^{-4}	KOt-Bu	3.2×10^{-3} methyl iodide	1.5	18	3.0
1.3×10^{-4}	5.2×10^{-4}	KOt-Bu	none	4	0	0[b]
2.2×10^{-4}	3.6×10^{-4}	phenyl lithium	none	2	98	0[c]

TABLE 4 (continued)

Moles of Nitro-olefin[a]	Moles of Base	Type of Base	Moles of Reagent Added	Reaction Time hrs.	% Nitro-olefin Unreacted	% Yield of Triene
2.2×10^{-4}	2.2×10^{-4}	phenyl lithium	none	5	100	0[d]
2.2×10^{-4}	8×10^{-4}	KOt-Bu	none	2	12	2.1[e]
2.2×10^{-4}	8×10^{-4}	KOt-Bu	none	2	11	1.8[f]
4.4×10^{-4}	2.25×10^{-3}	KOt-Bu	none	3	7.5	5.4
2.2×10^{-4}	9×10^{-4}	KOt-Bu	none	12	11	9.4[g]
2.2×10^{-4}	8×10^{-4}	KOt-Bu	none	2	14	3.5[h]
2.2×10^{-4}	8×10^{-4}	KOt-Bu	none	2	13	3.4[h]

[a] Unless otherwise stated the reactions were run using 10 ml. of heptane as solvent and 0.8 M potassium t-butoxide in t-butyl alcohol.

[b] Run with 0.026 molar solutions of potassium t-butoxide and 1,1-diphenyl-2-nitroethylene in tertiary butyl alcohol: benzophenone 100%.

[c] Run in 10 ml. of dry ether at room temperature using 0.36 M phenyl lithium in dry ether.

[d] Phenyl lithium (0.8 M in dry ether) added to 10 ml. of refluxing heptane solution in two equal aliquots one hour apart.

[e] Olefin added to a suspension of potassium t-butoxide in heptane.

[f] Potassium t-butoxide added to a solution of the olefin in heptane.

[g] Freshly prepared dry potassium t-butoxide added to a solution of the olefin in heptane.

[h] These two runs were exactly the same.

SUMMARY

1, 1-Diphenyl-2-nitroethylene(I) was found to produce benzo-
phenone(III), 1, 3-dinitro-2, 2-diphenylpropane(V), isobutylene(VI),
and 1, 1, 4, 4-tetraphenylbutatriene(IX) when reacted with the strong
base potassium t-butoxide. These products were accounted for on
the basis of two competing reactions. One involved a β-addition of
the butoxide ion to the starting material, followed by decomposition
of the resulting adduct to benzophenone(III), isobutylene(VI), and
nitromethane anion(IV). This anion could have added to 1, 1-diphenyl-
2-nitroethylene to produce 1, 3-dinitro-2, 2-diphenylpropane(V). The
other reaction involved a proton transfer from the starting material
to the basic potassium t-butoxide to produce a vinyl carbanion. This
carbanion could have undergone α-addition to 1, 1-diphenyl-2-nitro-
ethylene. The resulting adduct could have then undergone a series of
β-elimination reactions to produce 1, 1, 4, 4-tetraphenylbutatriene(IX).

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BIOGRAPHICAL ITEMS

Charles David Broaddus was born in Irvine, Kentucky on October 17, 1930. In 1952 he received the degree of Bachelor of Arts from Centre College in Danville, Kentucky and entered the graduate school of Alabama Polytechnic Institute in Auburn, Alabama. From that institution he received the degree of Master of Science in chemistry in August, 1954. After working for three years, he entered the graduate school of the University of Florida. During his graduate work at the University of Florida he has held a teaching assistantship, the Dupont teaching fellowship, and a Koppers research fellowship in the chemistry department.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.
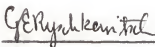
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